forded 40 mg. (5.5% yield based on acenaphthylene) of acenaphthylene-chromium tricarbonyl, a purple-black solid, decomposing near 175°, which gives intense violet solutions in organic solvents which are completely decolorized when exposed to air for several days. The acenaphthylene-chromium complex has carbonyl bands at 1970 and 1892 cm.$^{-1}$ in its infrared spectrum, and maxima in its ultraviolet spectrum (taken in cyclohexane) at 215 mμ (ϵ 38,500) and 349 mμ (ϵ 7420), with a minimum at 308 mμ (ϵ 3220).

Anal. Calcd. for $C_{15}H_{18}O_3Cr$: C, 62.5; H, 2.8. Found: C, 63.0; H, 3.1.

Acenaphthylene-Diiron Hexacarbonyl.—A mixture of triiron dodecacarbonyl (18.0 g., 35.6 mmoles), acenaphthylene (7.6 g., 50 mmoles) and 250 ml. of thiophene-free benzene was refluxed for 10 hr. under nitrogen. After cooling to room temperature, filtration gave a maroon filtrate which was evaporated to dryness. Sublimation at 60–70° (0.1 mm.) for 4 hr. led to the recovery of 4.2 g. (55%) of the acenaphthylene. The red-purple residue, 3.09 g. (32% yield based on acenaphthylene used), was fairly pure $C_{12}H_8Fe_2(CO)_6$. Part of this material (1.0 g.) was treated with a mixture of 25 ml. of petroleum ether and 20 ml. of diethyl ether and the resulting dark red solution filtered. The filtrate was evaporated to 10 ml. and cooled to −78°. The resulting purple crystals were filtered, recrystallized, and dried for 10 hr. at 25° (0.2 mm.). The acenaphthylene-diiron hexacarbonyl thus obtained melted sharply at 158°, and is a red-violet crystalline solid. The compound is stable in air for several months, but its solutions in organic solvents decompose in a few hours.

Anal. Calcd. for $C_{18}H_8O_6Fe_2$: C, 50.0; H, 1.85; mol. wt., 432. Found: C, 50.1, 50.4; H, 2.2, 2.2; mol. wt., 433.

The infrared spectrum of acenaphthylene-diiron hexacarbonyl shows carbonyl bands at 2047 and 1985 cm.$^{-1}$, and its ultraviolet spectrum (cyclohexane solution) has maxima at 227 mμ (ϵ 35,500) and 330 mμ (ϵ 10,500) with a minimum at 308 mμ.

Acknowledgment.—We are indebted to the Union Carbide Metals Co. for a gift of chromium hexacarbonyl, and to the Climax Molybdenum Co. for a gift of molybdenum and tungsten hexacarbonyls.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE UNIVERSITY]

Reactions of Silyl- and Germyllithium Compounds with Azoxybenzene

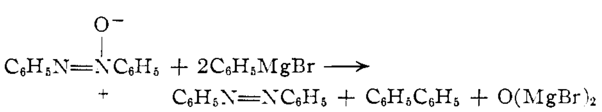
BY M. V. GEORGE, PURNENDU B. TALUKDAR, CLARE W. GEROW AND HENRY GILMAN

RECEIVED FEBRUARY 29, 1960

Reaction of triphenylsilyllithium with azoxybenzene gives N,N'-diphenyl-N-triphenylsilylhydrazine, a compound previously prepared by the direct addition of triphenylsilyllithium to azobenzene. Similarly, diphenylmethylsilyllithium and triphenylgermyllithium give N,N'-diphenyl-N-diphenylmethylsilylhydrazine and N,N'-diphenyl-N-triphenylgermylhydrazine, respectively. In these reactions it has been observed that azoxybenzene is first reduced to azobenzene which then reacts with the silyl- or germyllithium compound to give the corresponding addition products.

A number of studies concerned with the preparation and some of the reactions of silyl- and germylmetallic compounds have been reported in recent years.[1,2] The object of the present investigation was to study the reactions of silyl- and germyllithium compounds with azoxybenzene.

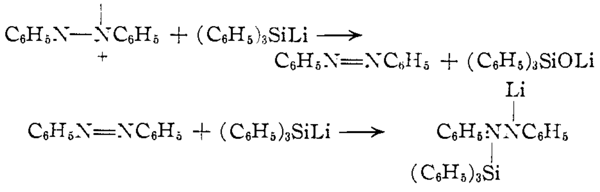
Kursanov, Kursanova and Blokhina[3] have reported the reaction of a number of azoxy compounds with Grignard reagents and have observed that these compounds were reduced to the corresponding azo compounds. Azoxybenzene, for example, on treatment with phenylmagnesium bromide, gave a 95.8% yield of azobenzene and also a 64.4% yield of biphenyl. A similar type of reduction of azoxy compounds was observed on treatment of these compounds with a mixture of magnesium and magnesium iodide.[4,5]



$$\underset{+}{C_6H_5N}{=}\overset{O^-}{N}C_6H_5 + 2C_6H_5MgBr \longrightarrow C_6H_5N{=}NC_6H_5 + C_6H_5C_6H_5 + O(MgBr)_2$$

It seemed of interest to study the reaction of silyl- and germyllithium compounds with azoxybenzene under conditions analogous to those of the reaction of Grignard reagents.

The reaction of a 2:1 mole ratio of triphenylsilyllithium with azoxybenzene gave a 52.9% yield of N,N'-diphenyl-N-triphenylsilylhydrazine.[6] In addition, an 11.0% yield of azobenzene and a 90.9% yield of triphenylsilanol were obtained. The first step in this reaction appears to be the reduction of azoxybenzene to azobenzene, which is immediately followed by the addition of triphenylsilyllithium across the nitrogen-nitrogen double bond in azobenzene giving N,N'-diphenyl-N-triphenylsilyl-N'-lithiohydrazine. The formation of a nearly quantitative yield of triphenylsilanol and the absence of any hexaphenyldisilane may be attributed to the great ease with which compounds containing silicon-oxygen bond are formed under these conditions.



$$\underset{+}{C_6H_5N}{-}\overset{O^-}{N}C_6H_5 + (C_6H_5)_3SiLi \longrightarrow C_6H_5N{=}NC_6H_5 + (C_6H_5)_3SiOLi$$

$$C_6H_5N{=}NC_6H_5 + (C_6H_5)_3SiLi \longrightarrow C_6H_5\underset{(C_6H_5)_3Si}{N}\overset{Li}{N}C_6H_5$$

When azoxybenzene and triphenylsilyllithium were allowed to react in a 1:1 mole ratio, the products isolated were N,N'-diphenyl-N-triphenylsilylhydrazine (26.8%), triphenylsilanol (14.5%) and

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(1) For a recent review on silylmetallic compounds, see, D. Wittenberg and H. Gilman, *Quart. Revs.*, **13**, 116 (1959).

(2) For an account of the preparation and some studies of germylmetallic compounds, see H. Gilman and C. W. Gerow, THIS JOURNAL, **77**, 4675, 5740 (1955); **78**, 5435 (1956); **79**, 342 (1957); *J. Org. Chem.*, **23**, 1582 (1958).

(3) D. N. Kursanov, A. S. Kursanova and A. N. Blokhina, *J. Gen. Chem.* (*U.S.S.R.*), **8**, 1786 (1938).

(4) H. Gilman and L. L. Heck, *Rec. trav. chim.*, **50**, 522 (1931).

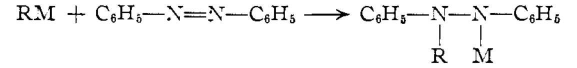
(5) W. A. Bachmann, THIS JOURNAL, **53**, 1524 (1931).

(6) D. Wittenberg, M. V. George, T. C. Wu, D. H. Miles and H. Gilman, *ibid.*, **80**, 4532 (1958).

azobenzene (22.0%). An appreciable amount of azoxybenzene (30.3%) was recovered unchanged. From this experiment, it is evident that the two reactions, namely, the reduction of azoxybenzene and addition of triphenylsilyllithium to azobenzene, take place almost simultaneously.

Similarly, the reaction of azoxybenzene with diphenylmethylsilyllithium in a 1:2 mole ratio gave a 53.8% yield of N,N′-diphenyl-N-diphenylmethylsilylhydrazine. The identity of this product was established by elemental analyses and also by infrared spectrum. The same compound was obtained in a 57.9% yield by treating azobenzene with diphenylmethylsilyllithium in a 1:1 mole ratio followed by the hydrolysis of the addition product.

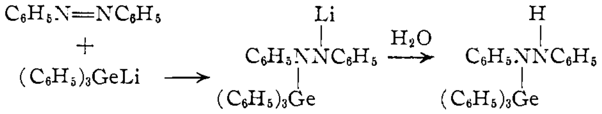
Triphenylgermyllithium apparently reacts with azo- and azoxybenzene in a manner indicative of its high degree of reactivity. It has been observed previously that only highly reactive organometallic compounds such as phenylcalcium iodide,[7] phenylpotassium[7] and diethylbarium[8] add to azo compounds to give unsymmetrically substituted hydrazines. A previous study[6] and the findings



$$RM + C_6H_5{-}N{=}N{-}C_6H_5 \longrightarrow C_6H_5{-}\underset{R}{\underset{|}{N}}{-}\underset{M}{\underset{|}{N}}{-}C_6H_5$$

from the present investigation show that silylmetallic compounds participate in such addition reactions to give silicon-substituted hydrazines.

When a 1:1 mole ratio of azobenzene and triphenylgermyllithium were allowed to react in tetrahydrofuran, a 58.0% yield of N,N′-diphenyl-N-triphenylgermylhydrazine, m.p. 142-143°, was obtained.



$$\begin{array}{l} C_6H_5N{=}NC_6H_5 \\ \quad + \\ (C_6H_5)_3GeLi \end{array} \longrightarrow C_6H_5\overset{Li}{\overset{|}{N}}\underset{(C_6H_5)_3Ge}{\underset{|}{N}}C_6H_5 \xrightarrow{H_2O} C_6H_5\overset{H}{\overset{|}{N}}\underset{(C_6H_5)_3Ge}{\underset{|}{N}}C_6H_5$$

From the reaction of triphenylgermyllithium and azoxybenzene, the products isolated were N,N′-diphenyl-N-triphenylgermylhydrazine (51.4%) and hexaphenyldigermoxane (83.1%). The formation of hexaphenyldigermoxane is accountable on the basis of the ready conversion of triphenylgermanol to hexaphenyldigermoxane. The reaction of triphenylgermyllithium with azoxybenzene appears to be similar to those of triphenylsilyllithium and other silylmetallic compounds.

The reactions of silyl- and germylmetallic compounds with azo and azoxy compounds give access to several interesting compounds, containing silicon-nitrogen and germanium-nitrogen bonds.

Experimental

All melting points are uncorrected. Reactions were carried out under an atmosphere of dry, oxygen-free[9] nitrogen. Tetrahydrofuran, boiling at 65–66°, was freed from peroxides and moisture before use by refluxing over sodium followed by distillation from lithium aluminum hydride. Triphenylsilyllithium and diphenylmethylsilyllithium solutions in tetrahydrofuran were prepared by lithium cleavage of the corresponding disilanes.[10] Silicon[11] and germanium[12] analyses were carried out by reported procedures.

Triphenylsilyllithium and Azoxybenzene.—A solution of 0.04 mole of triphenylsilyllithium in 80 ml. of tetrahydrofuran was added during 30 minutes to a stirred solution of 3.4 g. (0.02 mole) of azoxybenzene in 30 ml. of ether. The reaction was exothermic and the flask had to be cooled in a water-bath. The dark brown solution gave a negative Color Test I[13] when the addition was complete. The mixture was hydrolyzed by water and extracted with ether. The ether extract was dried over anhydrous sodium sulfate and the solvent removed by distillation. The residual oil was treated with cold methanol to give 5.9 g. of a yellow solid, m.p. 125–129°. Repeated crystallizations from a mixture of benzene and petroleum ether (b.p. 60–70°) gave 4.4 g. (52.9%) of N,N′-diphenyl-N-triphenylsilylhydrazine, m.p. 139–140°. The mixed melting point with an authentic sample[6] was not depressed. The infrared spectra of the two samples were also identical. The characteristic NH absorption band was observed at 3400 cm.$^{-1}$, whereas the Si-phenyl absorption band was found at 1110 cm.$^{-1}$.

The methanol-soluble portion was evaporated to give an orange-red solid which was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave 0.4 g. (11.0%) of azobenzene, m.p. and mixed m.p. 65–67°. Elution of the alumina column with methanol gave 5.0 g. (90.9%) of triphenylsilanol, which melted at 152–154°, after crystallization from a mixture of benzene and petroleum ether (b.p. 60–70°). A mixed melting point with an authentic sample of triphenylsilanol was not depressed.

In a second run using a 1:1 mole ratio of triphenylsilyllithium and azoxybenzene, the products isolated were 26.8% of N,N′-diphenyl-N-triphenylsilylhydrazine, 14.5% of triphenylsilanol, 22.0% of azobenzene and 30.3% of unchanged azoxybenzene.

Diphenylmethylsilyllithium and Azoxybenzene.—To a solution of 1.47 g. (0.0075 mole) of azoxybenzene in 25 ml. of ether, 0.015 mole of diphenylmethylsilyllithium in 70 ml. of tetrahydrofuran was added during 30 minutes. The deep brown solution gave a negative Color Test I[13] and was hydrolyzed with water. The hydrolyzed mixture was extracted with ether. Removal of the solvent from the dry ether extract gave a viscous oil, which solidified on treatment with cold methanol. Repeated crystallization of this material from a mixture of benzene and petroleum ether (b.p. 60–70°) gave 1.4 g. (53.8%) of N,N′-diphenyl-N-diphenylmethylsilylhydrazine, m.p. 119–120°. The infrared spectrum of this substance in carbon tetrachloride showed absorption bands at 3390 and 1112 cm.$^{-1}$, characteristic of NH and Si-phenyl groups, respectively.

Anal. Calcd. for $C_{25}H_{24}N_2Si$: C, 78.91; H, 6.36; N, 7.36. Found: C, 79.00, 79.10; H, 6.40, 6.50; N, 7.11, 7.33.

The methanol-soluble portion was evaporated and the residue obtained was chromatographed on alumina. Elution of the column with petroleum ether (b.p. 60–70°) gave 0.03 g. (2.2%) of azobenzene, m.p. and mixed m.p. 65–67°.

Diphenylmethylsilyllithium and Azobenzene.—A solution of 0.02 mole of diphenylmethylsilyllithium in 50 ml. of tetrahydrofuran was added to 3.64 g. (0.02 mole) of azobenzene, dissolved in 25 ml. of tetrahydrofuran, during 30 minutes. The solution gave a negative Color Test I.[13] The mixture was hydrolyzed with water and worked up as in the previous experiment to give 3.5 g. (57.9%) of N,N′-diphenyl-N-diphenylmethylsilylhydrazine, m.p. and mixed m.p. 119–120°, and 0.9 g. (24.7%) of unchanged azobenzene, m.p. and mixed m.p. 66–68°.

Triphenylgermyllithium and Azoxybenzene.—A solution of triphenylgermyllithium prepared by the cleavage of 12.1 g. (0.02 mole) of hexaphenyldigermane using 3.5 g. (0.5 g. atom) of lithium in 100 ml. of tetrahydrofuran was added to 3.96 g. (0.02 mole) of azoxybenzene dissolved in 30 ml. of ether, during 30 minutes. The solution became deep brown and Color Test I[13] was negative when the addition was complete. The reaction mixture was hydrolyzed with water and extracted with ether. The ether extract was dried over anhydrous sodium sulfate and the solvent was removed by distillation. The viscous oil obtained was treated with cold methanol to give 6.5 g. of a solid material, m.p. 130–132°. Several crystallizations from a mixture of benzene

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[7] H. Gilman and J. C. Bailie, *J. Org. Chem.*, **2**, 84 (1937).

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[10] H. Gilman and G. D. Lichtenwalter, THIS JOURNAL, **80**, 608 (1958).

[11] H. Gilman, B. Hofferth, H. W. Melvin, Jr., and G. E. Dunn, *ibid.*, **72**, 5767 (1950).

[12] H. Gilman and C. W. Gerow, *ibid.*, **77**, 5740 (1955).

[13] H. Gilman and F. Schulze, *ibid.*, **47**, 2002 (1925).

and petroleum ether (b.p. 60–70°) gave 5.0 g. (51.4%) of N,N′-diphenyl-N-triphenylgermylhydrazine, m.p. 142–143°. The infrared spectrum of this substance in carbon tetrachloride showed a strong absorption band at 3350 cm.$^{-1}$, characteristic of an NH group. Other prominent absorption bands were observed at 3080(s), 1590(s), 1485(s), 1430(s), 1270(s), 1095(s) and 1028(s) cm.$^{-1}$. The band at 1095 cm.$^{-1}$ appears to be due to Ge–phenyl group.

Anal. Calcd. for $C_{30}H_{26}N_2Ge$: C, 73.96; H, 5.38; N, 5.75; Ge, 14.9. Found: C, 73.39, 73.54; H, 5.44, 5.54; N, 5.80, 5.78; Ge, 15.18, 15.04.

The methanol solution on evaporation gave 5.8 g. of a solid melting at 177–179°. Crystallization from a toluene–petroleum ether (b.p. 60–70°) mixture gave 5.2 g. (83.1%) of hexaphenyldigermoxane, m.p. and mixed m.p. 187–189°.

The mother liquor after the removal of the digermoxane was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave 0.9 g. (24.7%) of azobenzene, m.p. and mixed m.p. 65–67°.

Triphenylgermyllithium and Azobenzene.—An ethylene glycol dimethyl ether solution of triphenylgermyllithium prepared by the cleavage of 7.6 g. (0.02 mole) of tetraphenylgermane with 2.0 g. (0.288 g. atom) of lithium[14] was added to 3.64 g. (0.02 mole) of azobenzene dissolved in 50 ml. of ethylene glycol dimethyl ether. The solution became deep brown and it was stirred at room temperature for 20 hr. It was then hydrolyzed by addition to a saturated ammonium chloride solution. The hydrolyzed mixture was extracted with ether, and removal of the solvent from the ether solution gave a residue which when treated with petroleum ether (b.p. 60–70°) gave 7.5 g. of a product melting at 139–141°. Recrystallization from a mixture of benzene and petroleum ether (b.p. 60–70°) gave 5.6 g. (58.0%) of N,N′-diphenyl-N-triphenylgermylhydrazine, m.p. 142–143°. The melting point was not depressed when admixed with an authentic sample of N,N′-diphenyl-N-triphenylgermylhydrazine, obtained from the previous reaction of azoxybenzene and triphenylgermyllithium. The infrared spectra of the two samples were also identical.

In a second run, using triphenylgermyllithium prepared by the lithium cleavage of hexaphenyldigermane in tetrahydrofuran, a 78.8% yield of N,N′-diphenyl-N-triphenylgermylhydrazine, m.p. 142–143°, was obtained.

Acknowledgment.—This research was supported by the United States Air Force under Contract AF 33(616)-3510 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright–Patterson AFB, Ohio. Infrared analyses were obtained through the courtesy of the Institute for Atomic Research, Iowa University, and special acknowledgment is made to Dr. V. Fassel and Mr. R. Kniseley for the spectra.

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[14] H. Gilman and C. W. Gerow, THIS JOURNAL, **77**, 4675 (1955).

[CONTRIBUTION FROM THE STAMFORD LABORATORIES, CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID CO., STAMFORD, CONN.]

Synthesis of Monoesters of Phosphonic Acids

BY ROBERT RABINOWITZ

RECEIVED FEBRUARY 19, 1960

Dialkyl esters of aryl- and alkylphosphonic acids, $RP(O)(OR')_2$, can be hydrolyzed smoothly, rapidly, and in high yield by refluxing in aqueous or ethanolic alkali. Furthermore O,O-diethyl phenylphosphonothioate, $C_6H_5P(S)(OC_2H_5)_2$, was found to hydrolyze to the monoester using *excess* ethanolic or aqueous base. Attempts to prepare the monoester of $CCl_3P(O)(OC_2H_5)_2$, using excess aqueous alkali failed. Finally hydrolysis of $C_6H_5P(O)(OC_6H_5)_2$ with excess alkali presumably resulted in phenylphosphonic acid. Mechanistic interpretations for these findings are presented.

No systematic study of the preparation of monoesters of phosphonic acids exists.[1] Some specific syntheses are known. For example, the reaction of $C_6H_5PCl_4$ with ethanol was reported to yield ethyl hydrogen phenylphosphonate, $C_6H_5P(O)(OC_2H_5)OH$[2]; $(C_6H_5)_3COH$ and PCl_3 react to form $(C_6H_5)_3COPCl_2$ which, when heated with 2.5 *N* alcoholic $NaOC_2H_5$, gave various proportions of phosphonic acid and its monoethyl ester, depending on the heating time.[3] Sarin, isopropyl methylphosphonofluoridate, $CH_3P(O)(F)(OC_3H_7\text{-}i)$, was hydrolyzed by a rat serum enzyme[4] to the monoester. Phenyl hydrogen phenylphosphonate was prepared by the reaction of $C_6H_5P(O)Cl_2$ with one mole of phenol to give $C_6H_5P(O)(OC_6H_5)Cl$ which was then hydrolyzed in H_2O to the desired product.[5] $HO_2C\text{–}CH_2CH_2P(O)(OC_2H_5)OH$ was reported as the product of acid or basic hydrolysis of the corresponding triethyl ester[6]; however, most acid hydrolyses of phosphonates yield the phosphonic acid.[7] $(C_2H_5O)_2P(O)CH_2OCH_2P(O)(OC_2H_5)_2$ and $C_6H_5CH_2OCH_2P(O)(OC_2H_5)_2$ were converted to the sodium salts of their monoesters when refluxed in ethanolic NaCl or NaBr. The free monoesters were not isolated[8a]; other Russian workers have used this alkali halide method to prepare salts of monoesters of phosphonic acids[8b,8c,8d,8e]; Chadwick[8f] used alkaline earth halides to prepare salts of monoesters of vinylphosphonic acid:

$$CaCl_2 + 2CH_2{=}CHP(O)(OC_2H_5)_2 \longrightarrow 2C_2H_5Cl + [CH_2{=}CHP(O)(OC_2H_5)O^-]_2Ca^{++}$$

Monoesters of trichloromethylphosphonic acid have received some attention. $CCl_3P(O)(OC_2H_5)OH$ was prepared by allowing the diester to stand in

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[1] When this work was essentially completed, a copy of a paper entitled, "The Preparation, Physical Properties, and Infrared Spectra of Several New Organophosphonates," by D. F. Peppard, J. R. Ferraro and G. W. Mason, which was presented at the March, 1959, Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, was secured. Monoesters of phosphonic acids were prepared in a manner analogous to that described in this paper; however, no duplication occurred.

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[4] F. C. G. Hoskin, *Can. J. Biochem. & Physiol.*, **34**, 75 (1956).

[5] A. Michaelis and K. Kammerer, *Ber.*, **8**, 1307 (1875).

[6] P. Nylen, *ibid.*, **59**, 1119 (1926).

[7] G. M. Kosalapoff, "Organophosphorus Compounds," J. Wiley and Sons, Inc., New York, N. Y., 1950.

[8] (a) V. S. Abramov, Ye. V. Sergeyeva and I. V. Chelpanova, *Zhur. Obshchei Khim.*, **14**, 1030 (1944); (b) V. S. Abramov and M. M. Azanovskaya, *ibid.*, **12**, 270 (1942); *C. A.*, **37**, 3048 (1943); (c) V. S. Abramov and E. A. Militskova, *ibid.*, **22**, 252 (1952); *C. A.*, **46**, 11100i (1952); (d) V. S. Abramov and M. N. Morozova, *ibid.*, **22**, 257 (1952); *C. A.*, **46**, 11099c (1952); (e) V. S. Abramov and O. D. Samoilova, *ibid.*, **22**, 914 (1952); *C. A.*, **47**, 4838d (1953); (f) P. H. Chadwick, U. S. Patent 2,784,206 (1957).